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Nonequilibrium molecular dynamics for bulk materials and nanostructures

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ABSTRACT

We describe a method of constructing exact solutions of the equations of molecular dynamics in non-equilibrium settings. These solutions correspond to some viscometric flows, and to certain analogs of viscometric flows for fibers and membranes that have one or more dimensions of atomic scale. This work generalizes the method of objective molecular dynamics (OMD) (Dumitrică and James, 2007). It allows us to calculate viscometric properties from a molecular-level simulation in the absence of a constitutive equation, and to relate viscometric properties directly to molecular properties. The form of the solutions is partly independent of the form of the force laws between atoms, and therefore these solutions have implications for coarse-grained theories. We show that there is an exact reduction of the Boltzmann equation corresponding to one family of OMD solutions. This reduction includes most known exact solutions of the equations of the moments for special kinds of molecules and gives the form of the molecular density function corresponding to such flows. This and other consequences leads us to propose an addition to the principle of material frame indifference, a cornerstone of nonlinear continuum mechanics. The method is applied to the failure of carbon nanotubes at an imposed strain rate, using the Tersoff potential for carbon. A large set of simulations with various strain rates, initial conditions and two choices of fundamental domain (unit cell) give the following unexpected results: Stone–Wales defects play no role in the failure (though Stone–Wales partials are sometimes seen just prior to failure), a variety of failure mechanisms is observed, and most simulations give a strain at failure of 15–20%, except those done with initial temperature above about 1200 K and at the lower strain rates. The latter have a strain at failure of 1–2%.

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1. Introduction

Among the most important deformations in solid mechanics are the bending, twisting and extension of beams. The most important flows in fluid mechanics are viscometric flows. In both cases these are the motions that, when compared with the corresponding experiments, are used to measure the material constants. In the simplest cases, these are elastic constants, viscosities and normal stress differences.

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In this paper we give a universal¹ molecular interpretation of these motions. From this viewpoint, the bending and twisting of a beam and the viscometric flow of a viscoelastic fluid, for example, are essentially the same. They both have an interpretation at atomic level as

$$\mathbf{y}_{g,k}(t) = g(\mathbf{y}_k(t)), \quad k = 1, \dots, M, \quad g \in G, \quad (1.1)$$

where G is a discrete group of isometries in three dimensions, and the $\mathbf{y}_k(t)$, $k = 1, \dots, M$ solve the equations of molecular dynamics. Taking $g = id$, we have that $\mathbf{y}_k(t) = \mathbf{y}_{id,k}(t)$. In the case of interest in this paper the elements $g \in G$ also have an explicit dependence on the time t . The group G typically has certain free parameters. The time dependence is introduced by allowing some of those parameters to depend on time in a particular way. Our main result is that, even though only $\mathbf{y}_1(t), \dots, \mathbf{y}_M(t)$ are assumed to satisfy the equations of molecular dynamics, all the typically infinite number of atoms with positions given by (1.1) necessarily satisfy those equations. Essentially, we identify a time-dependent invariant manifold² of these equations. The presence of this invariant manifold is a direct consequence of the frame-indifference and permutation invariance of the potential energy. These conditions on the atomic forces are satisfied quite generally, for example with a force on each nucleus given by the Hellmann–Feynman formula based on full (nonrelativistic) quantum mechanics under the Born–Oppenheimer assumption.

This justifies a numerical method in which only M atoms are simulated but all the atoms satisfy the equations of molecular dynamics. If the equations are exactly satisfied for the M atoms, then they are exactly satisfied by all³ the atoms. The number M and the initial conditions on the simulated atoms can be arbitrarily prescribed, independently of the group.

The case where the group elements do not depend explicitly on time has been studied in Dumitrică and James (2007) and Zhang et al. (2009). There it was shown how the bending, twisting and extension of nanoscale beams could be simulated by this method, and specific simulations were given for single-walled carbon nanotubes with atomic forces described by multi-body Tersoff (1988) potentials. Some interesting instabilities of the nanotubes were seen, including a regular rippling of the inside of the tube in pure bending and a helical rippling in torsion. These phenomena are very similar to those seen in experiment and captured by other methods, for example in the interesting papers of Arroyo and Arias (2008) and Yakobson et al. (1996). The present paper focuses on the case where the group elements have an explicit dependence on time.⁴ This corresponds to nanostructures that are out of equilibrium and, in the case of other groups (Section 6), to some classical viscometric flows.

As an example of the time-dependent case, we present calculations of carbon nanotubes extended at a constant strain rate (Section 8). A large set of simulations were done with various initial conditions, corresponding to initial temperatures between 300 and 1500 K, strain rates from 10^4 to 10^8 s^{-1} , and with two fundamental domains (unit cell) and their corresponding groups. We do not see any major differences between the results obtained with the two different fundamental domains. Several failure modes were noted, including melting, fibrous fracture, cavitation and cross-sectional collapse, but not the expected mechanism of the nucleation and glide of Stone–Wales defects. Occasionally, just prior to failure, we saw the formation of what could be termed Stone–Wales partials, but these quickly healed.⁵ We find that, for both fundamental domains and for all strain rates and initial temperatures, the strain at failure was in the range 15–20% for simulations with initial temperatures below about 1200 K. Near 1200 K and at the lower strain rates 10^4 – 10^6 s^{-1} there was a sharp drop of the strain at failure (to 1–2%). The strain rate had the unexpected effect of giving significantly higher elongation at higher rates. The failure at low strains was preceded by a large amplitude vibrations of the cross-section at a frequency of about 100 GHz.

While these preliminary serial simulations reach experimentally accessible rates at the lower end (10^4 s^{-1}), we are currently implementing parallel simulations that we estimate will reach strain rates that can be relatively easily imposed in experiments, permitting a direct comparison between predicted and measured failure modes and viscoelastic properties. This kind of direct comparison is a rarity in molecular dynamic simulations.

It is tempting to infer that these solutions for nanostructures have the same significance for the determination of molecular-level properties as viscometric flows do for bulk properties of fluids. Some solutions of the equations of molecular dynamics given by (1.1) have direct continuum analogs. Conversely, there are some well-studied viscometric flows in fluid mechanics, such as cone-and-plate flow, which are not given by (1.1). The latter arises partly from invariance assumed for the stress tensor in continuum mechanics that is not completely consistent with molecular dynamics.

Given a discrete isometry group, the construction of these solutions begins with the specification of the number M of simulated atoms and their initial conditions. As noted above, M can be any positive integer and the initial conditions are completely unrestricted. This raises the question of how many atoms are sufficient to capture representative behavior (in some precise sense) and what initial conditions are realistically permitted? In the case of periodic molecular dynamics,

¹ Here, universal means independent of the material.

² In the present context a time-dependent invariant manifold is a manifold in \mathbb{R}^{3MN} that depends on time and evolves in a prescribed way, independent of the solution. Under hypotheses of existence and uniqueness for the MD equations, a solution that begins on this manifold stays on this manifold for all time.

³ Typically, the isometry groups are infinite so there are infinitely many atoms altogether.

⁴ Even when the group elements do not depend on time, there are some large scale dynamic motions possible with OMD. For example, large scale coordinated radial vibrations of a carbon nanotube can be simulated with time-independent OMD. Results of some such simulations are given in Dumitrică and James (2007).

⁵ These results do not imply that Stone–Wales defects would also be absent in simulations at lower strain rates. Dumitrică et al. (2006) have given persuasive arguments based on energetics and statistical mechanics that these are likely at lower rates.

(which is a simple special case of OMD), if the supercell (i.e., M) is sufficiently large and the initial conditions are of sufficiently low total energy and correspond to the lattice parameters of the material being simulated, it is generally believed that the solutions obtained are in some sense statistically representative. In Dumitrică and James (2007) the dependence of the solutions on M and the initial conditions was also explored, and it was seen that different torsional instabilities could be expressed by different choices.

Another way to explore how representative are the solutions is to look for analogs in other theories of materials that are between molecular dynamics and continuum mechanics. We do this for the kinetic theory of gases. Based on special examples of the solutions found here, we develop an ansatz for the molecular density function and we show that there is an exact reduction of the Maxwell–Boltzmann equation corresponding to all these solutions. No assumptions on the atomic force laws are introduced. We also look at the H-theorem for these solutions, which has an interesting simple form. A detailed study of solutions of the reduced equation is given in a forthcoming paper (James and Müller).

The connection with the kinetic theory, and the fact that some aspects of these solutions are independent of the nature of the atomic forces, suggests that analogs of these solutions should be universally present in continuum theory. This assertion can be rephrased as a restriction on constitutive equations. The restriction arises essentially from the frame-indifference—actually, just the translation and permutation invariance—of the underlying potential energy. We argue in Section 7 that the present principle of material frame indifference of nonlinear continuum mechanics should be modified by the inclusion of these additional restrictions. All widely accepted constitutive equations satisfy the modified principle. The modified principle has interesting implications for some mesoscale theories (Section 7).

Notation: The summation convention is used here. \mathbb{Z} is the integers and \mathbb{Z}^3 is the set of triples of integers. Unless indicated otherwise, Greek letters are scalars and lower case Latin letters are vectors in \mathbb{R}^3 . Typically, uppercase Latin letters represent 3×3 matrices. \mathbf{A}^i denotes \mathbf{A} multiplied by itself i times, if i is a positive integer, or \mathbf{A}^{-1} multiplied by itself $|i|$ times if i is a negative integer. The letters \mathbf{Q} and \mathbf{R} , subscripted or not, are reserved for matrices in $O(3) = \{\mathbf{R} : \mathbf{R}^T \mathbf{R} = \mathbf{I}\}$; here, the superscript T indicates the transpose, and \mathbf{I} is the 3×3 identity matrix. $\mathbf{R}_\theta \in SO(3) = \{\mathbf{R} \in O(3) : \det \mathbf{R} = 1\}$ denotes a rotation of counterclockwise angle θ . Subscripts of vectors and matrices in this paper do not signify components; they are labels for atoms ($\mathbf{y}_{i,k}$ is the position vector of atom i, k).

2. Isometry groups and objective structures

The method relies on the use of discrete groups of isometries in three dimensions. The derivation of these groups is a classical topic (Opechowski, 1986). Some of them are summarized in the International Tables of Crystallography (Hahn, 2003). Of special interest for nanostructures are the *subperiodic groups*, that is, the groups that do not contain three linearly independent translations. Volume E of the International Tables contains an incomplete listing of the subperiodic groups. Another problem with the listings of these groups is that only the abstract groups are listed, whereas for the present method the explicit isometries, and particularly the allowed parameter dependence of these isometries, is needed. Motivated by these issues, we have calculated from the basic definition the explicit forms of all subperiodic, discrete groups of isometries in a forthcoming paper (Dayal et al.). We summarize here only the groups used in this paper.

A discrete group G of isometries in 3-D is assumed to consist of elements of the form $g = (\mathbf{Q}|\mathbf{c})$, $\mathbf{Q} \in O(3)$ and $\mathbf{c} \in \mathbb{R}^3$. Given $g_1 = (\mathbf{Q}_1|\mathbf{c}_1)$ and $g_2 = (\mathbf{Q}_2|\mathbf{c}_2)$, the rule for group multiplication is $g_1 g_2 = (\mathbf{Q}_1 \mathbf{Q}_2 | \mathbf{Q}_1 \mathbf{c}_2 + \mathbf{c}_1)$, and the rule for inverses is $g^{-1} = (\mathbf{Q}^T | -\mathbf{Q}^T \mathbf{c})$. These rules come from thinking about these isometries as acting on \mathbb{R}^3 : $g(\mathbf{x}) = \mathbf{Q}\mathbf{x} + \mathbf{c}$. Then composition of mappings gives

$$g_1(g_2(\mathbf{x})) = \mathbf{Q}_1(\mathbf{Q}_2\mathbf{x} + \mathbf{c}_2) + \mathbf{c}_1 = \mathbf{Q}_1\mathbf{Q}_2\mathbf{x} + \mathbf{Q}_1\mathbf{c}_2 + \mathbf{c}_1 = g_1 g_2(\mathbf{x}), \quad (2.1)$$

from which one can infer the rules for products and inverses given above. The identity is $id = (\mathbf{I}|0)$.

We shall often make use of the simplest isometry group, the 3-D translation group G_T . G_T is generated by the three elements $t_i = (\mathbf{I}|\mathbf{e}_i)$, $i = 1, 2, 3$ where $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ are linearly independent vectors (not necessarily orthogonal). It is given by

$$G_T = \{t_1^p t_2^q t_3^r : p, q, r \in \mathbb{Z}\} = \{(\mathbf{I}|p\mathbf{e}_1 + q\mathbf{e}_2 + r\mathbf{e}_3) : p, q, r \in \mathbb{Z}\}. \quad (2.2)$$

A general result from Dayal et al., that includes all other groups we shall use in this paper, is the following: if a discrete group of isometries does not contain a translation and does not consist entirely of rotations, it is expressible in one of the forms

$$\begin{aligned} G_1 &= \{h^p : p \in \mathbb{Z}\}, \\ G_2 &= \{h^p f^m : p \in \mathbb{Z}, m = 1, 2\}, \\ G_3 &= \{h^p g^q : p \in \mathbb{Z}, q = 1, \dots, n\}, \\ G_4 &= \{h^p g^q f^m : p \in \mathbb{Z}, q = 1, \dots, n, m = 1, 2\}, \end{aligned} \quad (2.3)$$

where

1. $h = (\mathbf{R}_\theta | \tau \mathbf{e} + (\mathbf{R}_\theta - \mathbf{I})\mathbf{x}_0)$, $\mathbf{R}_\theta \mathbf{e} = \mathbf{e}$, $|\mathbf{e}| = 1$, $\mathbf{x}_0 \cdot \mathbf{e} = 0$, $\mathbf{e}, \mathbf{x}_0 \in \mathbb{R}^3$, $\tau \neq 0$, and θ is an irrational multiple of 2π .
2. $g = (\mathbf{R}_\psi | (\mathbf{R}_\psi - \mathbf{I})\mathbf{x}_0)$, $\mathbf{R}_\psi \mathbf{e} = \mathbf{e}$, is a proper rotation with angle $\psi = 2\pi/n$, $n \in \mathbb{Z}$, $n \neq 0$.
3. $f = (\mathbf{R} | (\mathbf{R} - \mathbf{I})\mathbf{x}_1)$, $\mathbf{R} = -\mathbf{I} + 2\mathbf{e}_1 \otimes \mathbf{e}_1$, $|\mathbf{e}_1| = 1$, $\mathbf{e} \cdot \mathbf{e}_1 = 0$ and $\mathbf{x}_1 = \mathbf{x}_0 + \zeta \mathbf{e}$, for some $\zeta \in \mathbb{R}$.

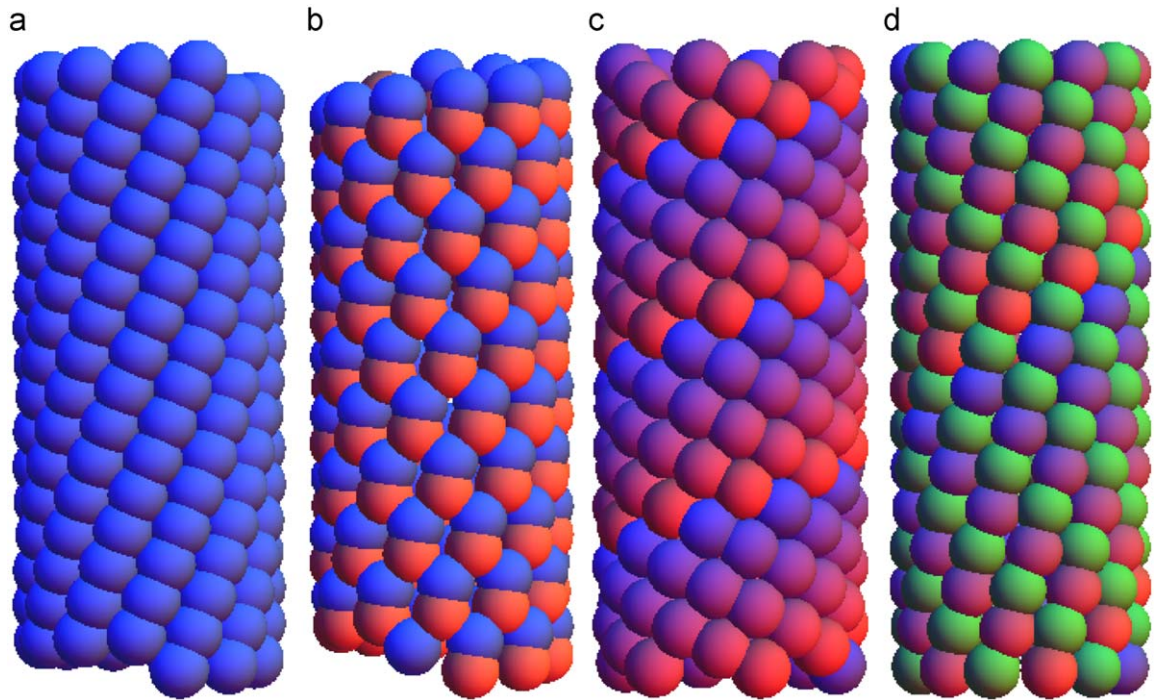


Fig. 1. Illustration of the four groups given by (2.3). The pictures are obtained by applying each of the groups to a single sphere. Coloring scheme is according to the powers of group elements, as noted. Group parameters conveniently chosen. (a) G_1 : all atoms blue; (b) G_2 : $m = 1$ red; $m = 2$ blue; (c) G_3 : $n = 6$; shading proportional to q ; (d) G_4 : $n = 6$; $m = 1$ green; $m = 2$ red/blue, shading proportional to q . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The isometries h, g, f having these forms necessarily satisfy $gh = hg, fh = h^{-1}f$ and $fg = g^{-1}f$. Conversely, if the elements h, g, f satisfy 1–3, then the sets given in (2.3) are discrete groups of isometries with no translation. If θ is instead chosen to be a rational multiple of 2π , but all else is the same, then (2.3) also gives discrete groups of isometries, but these then contain a one-dimensional translational subgroup. Our examples of Section 8 are of this latter type.

With appropriate choices of the parameters the group $\{h^p g^q f^m : p \in \mathbb{Z}, q = 1, \dots, n, m = 1, 2\}$, operating on a single point in \mathbb{R}^3 , describes the structures of single walled carbon nanotubes of any chirality.⁶

In Section 8, as an illustration of the use of OMD for simulating the viscometry of nanostructures, we use groups having the forms of G_2 and G_3 listed in (2.3). The detailed choice of parameters is given in Section 8, but we here give an overview of how the groups and parameters were chosen. We first used the group $G_4 = \{h^p g^q f^m : p \in \mathbb{Z}, q = 1, \dots, n, m = 1, 2\}$, operating on an appropriate point $\mathbf{z}_1 \in \mathbb{R}^3$ to generate a static carbon nanotube with near the relaxed lattice parameter at zero temperature,⁷ as done schematically in Fig. 1. In Section 8 this is chosen as a (6,6) nanotube. Then we chose a pair of integers p', q' with q' dividing n with no remainder, and we defined $h' = h^{p'}, g' = g^{q'}$. The subgroup $G' = \{h'^p g'^q : p \in \mathbb{Z}, q = 1, \dots, n/q'\}$ generates exactly the same static nanotube, not when applied to a single point in \mathbb{R}^3 , but when applied to a certain set S of $2p'q'$ points.⁸ In fact this set of points is given by $S = \{h^p g^q f^m(\mathbf{z}_1) : p = 1, \dots, p', q = 1, \dots, q', m = 1, 2\}$. We chose S as the initial positions of our $M = 2p'q'$ simulated atoms. This procedure works for nanotubes of any chirality and any subgroup: one simply changes the values of parameters. The initial positions are those of the nominally relaxed nanotube with that chirality and subgroup.

The initial velocities of these simulated atoms were chosen to give various initial temperatures, after a transient. In preliminary simulations we found that the entire nanotube often spun rapidly about its axis with approximately constant angular velocity. After that, and in all simulations reported, the initial velocities were chosen to have total initial angular velocity zero. The method of simulation is described in detail in the next section.

Objective structures as defined in James (2006) are molecular structures consisting of a set of N identical molecules, each having M atoms, in which corresponding atoms in each molecule see the same environment. That is, the atomic

⁶ As well as structures obtained by uniformly twisting or extending them.

⁷ The precise value is not important, as the method allows for relaxation of lattice parameters. However, one should keep in mind that the state of the nanotube, after the inevitable transient, may be axially stressed.

⁸ This set of points belongs to the *fundamental domain* FD of the group G' , that is, a domain such that G' acting on the FD covers \mathbb{R}^3 and images of the FD under G' do not overlap.

environments of two corresponding atoms can be mapped into each other by an orthogonal transformation. “Corresponding atoms” can be taken to be the i th atoms of each molecule, and these statements are required to hold for every $i \in \{1, \dots, M\}$. It is shown in Dayal et al. that, after possibly renumbering the molecules, every discrete objective structure can be written as a discrete isometry group applied to the positions of a single molecule. It is then seen that OMD is a method of simulation for objective structures, although the simulated atoms would rarely be chosen to represent an actual physical molecule.

3. Objective molecular dynamics with time-dependent groups

Given a discrete group of isometries $G = \{g_1, g_2, \dots, g_N\}$, $g_1 = id$, let the *simulated atoms* be denoted as above by $\mathbf{y}_k(t)$, $k = 1, \dots, M$ with corresponding masses m_1, \dots, m_M . Typically, we will have $N = \infty$ but M is assumed to be finite. All other atoms of the structure will have positions given by

$$\mathbf{y}_{i,k}(t) = g_i(\mathbf{y}_k(t)), \quad g_i \in G, \quad i = 1, \dots, N, \quad k = 1, \dots, M. \quad (3.1)$$

Keep in mind that we are interested in the case that the elements $g \in G$ depend explicitly on time even though this is suppressed in the notation. We will assume that for any $i = 1, \dots, N$ the species of $\mathbf{y}_{i,k}(t)$ is the same as the species of $\mathbf{y}_k(t)$, that is, that all atoms labelled i, k have mass m_k and an atomic number that depends only on k .

The force on atom i, k is denoted by the suggestive notation $-\partial\varphi/\partial\mathbf{y}_{i,k} : \mathbb{R}^{3MN} \rightarrow \mathbb{R}^3$. We assume that this function is smooth and frame-indifferent, i.e., for all $\mathbf{Q} \in O(3)$ and $\mathbf{c} \in \mathbb{R}^3$,

$$\mathbf{Q} \frac{\partial\varphi}{\partial\mathbf{y}_{i,k}}(\dots, \mathbf{y}_{i_1,1}, \dots, \mathbf{y}_{i_1,M}, \dots, \mathbf{y}_{i_2,1}, \dots, \mathbf{y}_{i_2,M}, \dots) = \frac{\partial\varphi}{\partial\mathbf{y}_{i,k}}(\dots, \mathbf{Q}\mathbf{y}_{i_1,1} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{y}_{i_1,M} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{y}_{i_2,1} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{y}_{i_2,M} + \mathbf{c}, \dots), \quad (3.2)$$

and also that it is permutation invariant,

$$\frac{\partial\varphi}{\partial\mathbf{y}_{\Pi(i,k)}}(\dots, \mathbf{y}_{i_1,1}, \dots, \mathbf{y}_{i_1,M}, \dots, \mathbf{y}_{i_2,1}, \dots, \mathbf{y}_{i_2,M}, \dots) = \frac{\partial\varphi}{\partial\mathbf{y}_{i,k}}(\dots, \mathbf{y}_{\Pi(i_1,1)}, \dots, \mathbf{y}_{\Pi(i_1,M)}, \dots, \mathbf{y}_{\Pi(i_2,1)}, \dots, \mathbf{y}_{\Pi(i_2,M)}, \dots), \quad (3.3)$$

where Π is any permutation that preserves species. Here, preservation of species means that if $(i, k) = \Pi(j, \ell)$ then the species (i.e., atomic mass and number) of atom i, k is the same as the species of atom j, ℓ . These invariances are formally satisfied, for example, by the Hellmann–Feynman force formula based on Born–Oppenheimer quantum mechanics.

The conditions (3.2), (3.3) can be found by formally differentiating the conditions of frame-indifference and permutation invariance of the potential energy,

$$\begin{aligned} \varphi(\dots, \mathbf{y}_{i_1,1}, \dots, \mathbf{y}_{i_1,M}, \dots, \mathbf{y}_{i_2,1}, \dots, \mathbf{y}_{i_2,M}, \dots) &= \varphi(\dots, \mathbf{y}_{\Pi(i_1,1)}, \dots, \mathbf{y}_{\Pi(i_1,M)}, \dots, \mathbf{y}_{\Pi(i_2,1)}, \dots, \mathbf{y}_{\Pi(i_2,M)}, \dots) \\ &= \varphi(\dots, \mathbf{Q}\mathbf{y}_{i_1,1} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{y}_{i_1,M} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{y}_{i_2,1} + \mathbf{c}, \dots, \mathbf{Q}\mathbf{y}_{i_2,M} + \mathbf{c}, \dots) \end{aligned} \quad (3.4)$$

with respect to $\mathbf{y}_{i,k}$. However, in the present situation it is preferable to assume the invariance condition at the level of the forces, as the potential energy is typically infinite when $N = \infty$, whereas the forces are finite and satisfy the invariance conditions given above under mild conditions on the atomic positions.

Note that we use the full orthogonal group here, as this is the invariance group of Born–Oppenheimer quantum mechanics. In continuum mechanics people often restrict invariance to proper rotations, but this restriction arises essentially because continuum mechanics deals with relatively smooth families of deformations rather than atomic positions.

In addition to the two invariances given above, we make the essential hypothesis that the time dependence of every element in G is such that

$$\frac{d^2\mathbf{y}_{j,k}(t)}{dt^2} = \frac{d^2}{dt^2} g_j(\mathbf{y}_k(t)) = \mathbf{Q}_j \frac{d^2\mathbf{y}_k(t)}{dt^2}, \quad g_j = (\mathbf{Q}_j | \mathbf{c}_j) \in G, \quad j = 1, \dots, N, \quad k = 1, \dots, M. \quad (3.5)$$

Now consider any particular isometry $g = (\mathbf{Q} | \mathbf{c}) \in G$. Because G is a group, if we apply g to the structure defined by (3.1), i.e., we calculate $g(\mathbf{y}_{i,k}(t))$, $i = 1, \dots, N$, $k = 1, \dots, M$, we recover exactly the same structure back again. (Both g and g_i here are evaluated also at time t .) Thus, there must be a permutation Π , depending on the choice of g , such that

$$\mathbf{y}_{\Pi(i,k)}(t) = g(\mathbf{y}_{i,k}(t)), \quad i = 1, \dots, N, \quad k = 1, \dots, M. \quad (3.6)$$

Now fix $j \in \{1, \dots, N\}$ and choose $g = g_j^{-1} = (\mathbf{Q}_j^T | -\mathbf{Q}_j^T \mathbf{c}_j)$. The corresponding permutation Π satisfies $\Pi(j, k) = (1, k)$, by (3.6) and (3.1). Now assume that $\mathbf{y}_1(t), \dots, \mathbf{y}_M(t)$ satisfy the equations of molecular dynamics, i.e.,

$$\begin{aligned} m_k \ddot{\mathbf{y}}_k(t) &= -\frac{\partial\varphi}{\partial\mathbf{y}_{1,k}}(\dots, \mathbf{y}_{i_1,1}(t), \dots, \mathbf{y}_{i_1,M}(t), \mathbf{y}_{i_2,1}(t), \dots, \mathbf{y}_{i_2,M}(t), \dots) \\ &= -\frac{\partial\varphi}{\partial\mathbf{y}_{1,k}}(\dots, g_i(\mathbf{y}_1(t)), \dots, g_i(\mathbf{y}_M(t)), g_{i+1}(\mathbf{y}_1(t)), \dots, g_{i+1}(\mathbf{y}_M(t)), \dots). \end{aligned} \quad (3.7)$$

Together with initial conditions on the M simulated atoms,

$$\mathbf{y}_k(0) = \mathbf{y}_k^0, \quad \dot{\mathbf{y}}_k(0) = \mathbf{v}_k^0, \quad k = 1, \dots, M, \quad (3.8)$$

this is an ordinary differential system in standard form. Using the full invariance (3.2), (3.3), the condition $\Pi(j, k) = (1, k)$, and the assumption (3.5), we have that

$$\begin{aligned} m_k \ddot{\mathbf{y}}_{j,k}(t) &= m_k \mathbf{Q}_j \ddot{\mathbf{y}}_k(t) = -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{1,k}}(\dots, \mathbf{y}_{i,1}(t), \dots, \mathbf{y}_{i,M}(t), \mathbf{y}_{i+1,1}(t), \dots, \mathbf{y}_{i+1,M}(t), \dots) \\ &= -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{\Pi(j,k)}}(\dots, \mathbf{y}_{i,1}(t), \dots, \mathbf{y}_{i,M}(t), \mathbf{y}_{i+1,1}(t), \dots, \mathbf{y}_{i+1,M}(t), \dots) \\ &= -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\dots, \mathbf{y}_{\Pi(i,1)}(t), \dots, \mathbf{y}_{\Pi(i,M)}(t), \dots, \mathbf{y}_{\Pi(i+1,1)}(t), \dots, \mathbf{y}_{\Pi(i+1,M)}(t), \dots) \\ &= -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\dots, g_j^{-1}(\mathbf{y}_{i,1}(t)), \dots, g_j^{-1}(\mathbf{y}_{i,M}(t)), g_j^{-1}(\mathbf{y}_{i+1,1}(t)), \dots, g_j^{-1}(\mathbf{y}_{i+1,M}(t)), \dots) \\ &= -\mathbf{Q}_j \frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\dots, \mathbf{Q}_j^T \mathbf{y}_{i,1}(t) - \mathbf{Q}_j^T \mathbf{c}_j, \dots, \mathbf{Q}_j^T \mathbf{y}_{i,M}(t) - \mathbf{Q}_j^T \mathbf{c}_j, \mathbf{Q}_j^T \mathbf{y}_{i+1,1}(t) - \mathbf{Q}_j^T \mathbf{c}_j, \dots, \mathbf{Q}_j^T \mathbf{y}_{i+1,M}(t) - \mathbf{Q}_j^T \mathbf{c}_j, \dots) \\ &= -\frac{\partial \varphi}{\partial \mathbf{y}_{j,k}}(\dots, \mathbf{y}_{i,1}(t), \dots, \mathbf{y}_{i,M}(t), \mathbf{y}_{i+1,1}(t), \dots, \mathbf{y}_{i+1,M}(t), \dots). \end{aligned} \quad (3.9)$$

This shows that all the other atoms also satisfy the equations of molecular dynamics.

In simulations, the atoms with positions $\mathbf{y}_1, \dots, \mathbf{y}_M$ will be simulated and other atoms will be forced to go to locations determined by (3.1). The force on each of the atoms $\mathbf{y}_1, \dots, \mathbf{y}_M$ is calculated from all the other atoms.

4. Allowed time dependence of the group elements

Here we study the condition (3.5). Writing $g_j = (\mathbf{Q}_j | \mathbf{c}_j)$, $\mathbf{Q}_j \in O(3)$, $\mathbf{c}_j \in \mathbb{R}^3$, we allow $\mathbf{Q}_j, \mathbf{c}_j$ to depend on t and we write $(d/dt)\mathbf{Q}_j = \mathbf{Q}_j \mathbf{W}_j$ (no sum), where $\mathbf{W}_j = -\mathbf{W}_j^T$. Then the condition (3.5) is

$$\frac{d^2}{dt^2}(\mathbf{Q}_j \mathbf{y}_k + \mathbf{c}_j) = \mathbf{Q}_j \frac{d^2 \mathbf{y}_k(t)}{dt^2}, \quad (4.1)$$

that is,

$$\mathbf{Q}_j \mathbf{W}_j^2 \mathbf{y}_k + \mathbf{Q}_j \dot{\mathbf{W}}_j \mathbf{y}_k + +2\mathbf{Q}_j \mathbf{W}_j \dot{\mathbf{y}}_k + \mathbf{Q}_j \ddot{\mathbf{y}}_k + \ddot{\mathbf{c}}_j = \mathbf{Q}_j \ddot{\mathbf{y}}_k, \quad (4.2)$$

or, equivalently,

$$\ddot{\mathbf{c}}_j = -\mathbf{Q}_j (\mathbf{W}_j^2 \mathbf{y}_k + \dot{\mathbf{W}}_j \mathbf{y}_k + 2\mathbf{W}_j \dot{\mathbf{y}}_k). \quad (4.3)$$

This condition is highly restrictive, since it must be satisfied for every $k = 1, \dots, M$ and also for every $t > 0$ (It is not sufficient that it be satisfied in a statistical or average sense). Unless the initial conditions are extremely special, the values of \mathbf{y}_k and $\dot{\mathbf{y}}_k$ will fluctuate erratically; in addition, M is usually larger than the number of unknowns (= 6) in (4.3). Thus, as a useful condition for molecular dynamics, it only makes sense to solve (4.3) in the case that \mathbf{y}_k and $\dot{\mathbf{y}}_k$ are independently assignable vectors in \mathbb{R}^3 at each $t > 0$. We have that (4.3) is satisfied for independent choices of $\mathbf{y}_k, \dot{\mathbf{y}}_k$ if and only if

$$\ddot{\mathbf{c}}_j = 0 \quad \text{and} \quad \mathbf{W}_j = 0, \quad t > 0. \quad (4.4)$$

That is, $\mathbf{Q}_j \in O(3)$ must be constant and $\mathbf{c}_j = \mathbf{a}_j t + \mathbf{b}_j$ must be an affine function of t . In short, each group element is a Galilean transformation. This condition does not imply that the entire collection of atoms undergoes a Galilean transformation, and these conditions still lead to many interesting groups corresponding to a variety of flowing structures.

A simple but important observation is that the rules for multiplication and inversion of isometries given in Section 2 have the property that if two isometries have affine dependence of their translation on t , then so do their product and inverses. Hence, necessary and sufficient conditions for a group of isometries to consist of elements whose translations are affine in t is that the translations of the generators of that group have affine dependence on t .

For the groups used in OMD simulations of carbon nanotubes (see Sections 2, 8) the affine dependence on t is introduced by allowing τ in the generator h defined after (2.3) to be given as $\tau = \tau_0(1 + \dot{\epsilon}t)$. With this choice a typical evolution is shown in Fig. 2. Here τ_0 is chosen to correspond to the relaxed nanotube as described at the end of Section 2, and $\dot{\epsilon}$ has the direct interpretation as the imposed axial strain rate.

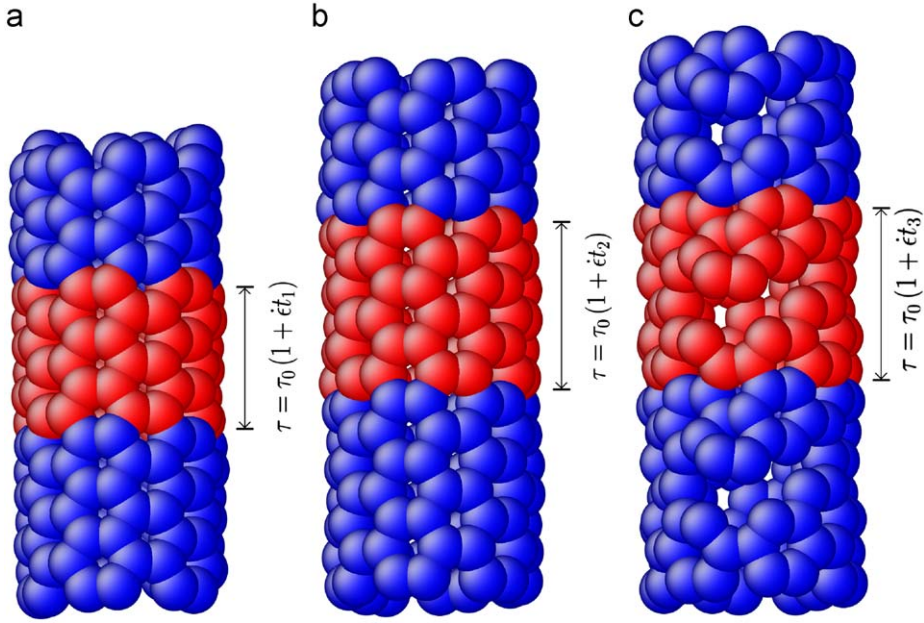


Fig. 2. Illustration of an OMD simulation of a carbon nanotube pulled at constant strain rate. The red atoms are simulated and lie in the fundamental domain. The corresponding group is G_I in (2.3). Values of the parameters are given in Section 8. (a) $t_1 = 20$ ps; (b) $t_2 = 1730$ ps; (c) $t_3 = 2240$ ps. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Simplest case corresponding to the translation group

5.1. Description of the method

This is the simplest case of the method, and the case that relates directly with viscometric flows of (typically, non-Newtonian) fluids. The positions of all the atoms are given by

$$\mathbf{y}_{v,k}(t), \quad v \in \mathbb{Z}^3, \quad k = 1, \dots, M, \quad t > 0. \quad (5.1)$$

where \mathbb{Z}^3 denotes all triples of integers. For convenience, and in view of (2.2), we now index the group elements by triples of integers $v = (v^1, v^2, v^3)$ with the identity element associated to $(0,0,0)$. The simulated atoms will undergo motions given by $\mathbf{y}_k(t) = \mathbf{y}_{(0,0,0),k}(t)$, $k = 1, \dots, M$. The group is G_T given by (2.2) except that we replace \mathbf{e}_i by $\mathbf{e}_i + t\tilde{\mathbf{e}}_i$, so as to be consistent with the conclusions of the last section. To make comparisons with continuum and kinetic theories easier, we write $\tilde{\mathbf{e}}_i = \mathbf{A}\mathbf{e}_i$, $i = 1, 2, 3$, for some linear transformation \mathbf{A} , without loss of generality. It is then immediately seen that all elements of G_T have affine time-dependence, so the theorem of the preceding section holds. The atoms that are not simulated will be forced to adopt positions given in terms of the simulated atoms by

$$\mathbf{y}_{\mu,k}(t) = g_{\mu}(\mathbf{y}_k(t)) = \mathbf{y}_k(t) + \mu^i \mathbf{e}_i + \mu^i t \mathbf{A}\mathbf{e}_i = \mathbf{y}_k(t) + (\mathbf{I} + t\mathbf{A})(\mu^i \mathbf{e}_i), \quad (5.2)$$

where $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ are three linearly independent vectors, \mathbf{A} is a linear transformation and $\mu \in \mathbb{Z}^3$. The quantities \mathbf{A} and the linearly independent $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ are assignable, but they cannot depend on the time t , so that the only time dependence is that shown explicitly on the right hand side of (5.2). The atom (μ, k) is also assumed to be of the same species as the simulated atom $((0, 0, 0), k)$.

5.2. Viscometry in fluid mechanics

The relation with fluid mechanics is the following. Typically the linearly independent vectors $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ will be chosen as small multiples of molecular dimensions, say, roughly 1–100 times the size of a molecule. For suitable choices of the integers (μ^1, μ^2, μ^3) , a given vector in \mathbb{R}^3 can then be approximated by $\mu^i \mathbf{e}_i$ up to an error of molecular dimensions. We can think of a continuum Lagrangian variable \mathbf{x} as being well approximated by $\mu^i \mathbf{e}_i$ for some choice of $\mu \in \mathbb{Z}^3$. Without loss of generality we can assume that the simulated atoms $\mathbf{y}_i(t)$ belong to the unit cell $\mathcal{U}(t) = \{\lambda^i (\mathbf{I} + t\mathbf{A})\mathbf{e}_i : 0 \leq \lambda^i < 1, i = 1, 2, 3\}$ attached to the origin. Occasionally it may happen that a simulated atom leaves $\mathcal{U}(t)$ (which causes no problem). At the same instant an atom of the same species enters $\mathcal{U}(t)$ with a different velocity from the one that left, according to (5.2). If one wishes one can occasionally redefine the simulated atoms to lie in $\mathcal{U}(t)$. We thus see that (5.2) is analogous to the

Lagrangian description of the motion

$$\mathbf{y}(\mathbf{x}, t) = (\mathbf{I} + t\mathbf{A})\mathbf{x}. \quad (5.3)$$

These are affine motions. The subsections above give a molecular level interpretation of these flows for any choice of the matrix \mathbf{A} . The relation to viscometric flows of Navier–Stokes or non-Newtonian fluids is the following. The constitutive theory of both kinds of fluids can be subsumed under the theory of incompressible *simple fluids*. These are materials governed by a constitutive equation for the Cauchy stress of the general form

$$\boldsymbol{\sigma}(\mathbf{y}, t) = -p\mathbf{I} + \Sigma(\mathbf{F}_t(\mathbf{y}, \cdot)), \quad (5.4)$$

where Σ is a functional that operates on “histories”, that is, it operates on 3×3 matrix-valued functions of the form $\mathbf{F}_t(\mathbf{y}, \tau)$, $\tau \leq t$, with determinant 1, and with t, \mathbf{y} being parameters. The function $\mathbf{F}_t(\mathbf{y}, \tau)$, $\tau \leq t$, $\mathbf{y} \in \Omega_t$, is the *relative deformation gradient*, i.e., it is the gradient of the deformation that maps the domain Ω_t of the body at time t to its domain Ω_τ at the earlier time τ . That is, $\mathbf{F}_t(\mathbf{z}, \tau)$ is the gradient with respect to \mathbf{z} of the function $\mathbf{y}(\mathbf{y}^{-1}(\mathbf{z}, t), \tau)$, where $\mathbf{y}(\mathbf{x}, t)$ is an ordinary Lagrangian description of motion for example as given in (5.3). The scalar p is the pressure. *Viscometric flows* are defined by the following restriction on the relative deformation gradient:

$$\mathbf{F}_t(\mathbf{y}, \tau) = \mathbf{Q}_t(\mathbf{y}, \tau)(\mathbf{I} + (\tau - t)\mathbf{M}_t(\mathbf{y})), \quad \mathbf{M}_t^2 = \mathbf{0}, \mathbf{Q}_t \in \text{O}(3), \tau \leq t, t > 0, \mathbf{y} \in \Omega_t, \quad (5.5)$$

(see, e.g., Coleman et al., 1966⁹). We note that the condition $\mathbf{M}_t^2 = \mathbf{0}$ is necessary and sufficient that \mathbf{M}_t is expressible¹⁰ in the form $\mathbf{M}_t = \mathbf{a}_t \otimes \mathbf{b}_t$ with $\mathbf{a}_t \cdot \mathbf{b}_t = 0$. With this form of \mathbf{M}_t the constraint of incompressibility is necessarily satisfied by viscometric flows.

The relative deformation gradient of the affine motion (5.3) is by direct calculation¹¹

$$\mathbf{F}_t(\mathbf{y}, \tau) = (\mathbf{I} + \tau\mathbf{A})(\mathbf{I} + t\mathbf{A})^{-1}. \quad (5.6)$$

Comparing (5.6) to (5.5), in particular, putting $\mathbf{F}_t^T \mathbf{F}_t$ from (5.6) equal to the same quantity based on (5.5) and then evaluating at $t = 0$, we see after a few calculations that the affine motion (5.3) describes a viscometric flow if and only if $\mathbf{A} = \mathbf{M}_0 = \mathbf{a} \otimes \mathbf{b}$, $\mathbf{a} \cdot \mathbf{b} = 0$, in which case $\mathbf{F}_t(\mathbf{y}, \tau) = \mathbf{I} + (\tau - t)\mathbf{a} \otimes \mathbf{b}$. This is the case of plane Couette flow. That is, if $\mathbf{A} = \mathbf{a} \otimes \mathbf{b}$, $\mathbf{a} \cdot \mathbf{b} = 0$ then the Eulerian velocity based on (5.3) is

$$\mathbf{v}(\mathbf{z}, t) = \dot{\mathbf{y}}(\mathbf{y}^{-1}(\mathbf{z}, t), t) = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{z} = \mathbf{a}(\mathbf{b} \cdot \mathbf{z}). \quad (5.7)$$

That is, in the orthonormal basis aligned with $\{\mathbf{a}, \mathbf{b}, \mathbf{a} \times \mathbf{b}\}$, we have $\mathbf{v} = (\kappa z_2, 0, 0)$.

On the other hand, there are flows of the form (5.6) in an incompressible fluid that are not viscometric flows. To see this, we impose only the condition of incompressibility on (5.6). This condition, $\det \mathbf{F}_t(\mathbf{y}, \tau) = 1$ for all $\tau \leq t > 0$, is equivalent to $\det(\mathbf{I} + \mathbf{A}t) = 1$ for all $t > 0$. Divide this by t^3 and look at the characteristic equation to prove that necessary and sufficient conditions for $\det(\mathbf{I} + \mathbf{A}t) = 1$ for all $t > 0$ are that $\det \mathbf{A} = \text{tr} \mathbf{A} = \text{tr} \mathbf{A}^2 = 0$. In turn, a necessary and sufficient condition that $\det \mathbf{A} = \text{tr} \mathbf{A} = \text{tr} \mathbf{A}^2 = 0$ is that there is an orthonormal basis such that in this basis \mathbf{A} has the form

$$\mathbf{A} = \begin{pmatrix} 0 & 0 & \kappa \\ \gamma_1 & 0 & \gamma_3 \\ 0 & 0 & 0 \end{pmatrix}. \quad (5.8)$$

Generally, this is a rank-2 matrix. Thus there are many isochoric affine flows that are not viscometric flows.

Based on the known relation between molecular dynamics and continuum mechanics, either via the kinetic theory or by spatial averaging (Noll, 1955; Irving and Kirkwood, 1950; Hardy, 1982; Murdoch and Bedeaux, 1994), we expect that the affine flows will have a favorable relation to the balance laws of continuum mechanics. Note that \mathbf{F}_t given by (5.6) is independent of \mathbf{y} . For all other constitutive relations of which we are aware (see Section 7) the Cauchy stress based on an affine motion is uniform in space. Therefore, the balance of linear momentum becomes

$$\rho(\mathbf{v}_t + \nabla \mathbf{v} \mathbf{v}) = \nabla \cdot \boldsymbol{\sigma} = \mathbf{0}. \quad (5.9)$$

This equation is identically satisfied for all affine motions, because, using the Eulerian velocity (5.7),

$$\rho(\mathbf{v}_t + \nabla \mathbf{v} \mathbf{v}) = \rho(-\mathbf{A}(\mathbf{I} + \mathbf{A}t)^{-1}\mathbf{A}(\mathbf{I} + \mathbf{A}t)^{-1}\mathbf{y} + \mathbf{A}(\mathbf{I} + \mathbf{A}t)^{-1}\mathbf{A}(\mathbf{I} + \mathbf{A}t)^{-1}\mathbf{y}) = \mathbf{0}. \quad (5.10)$$

Now we can interpret these calculations. The presence of \mathbf{Q}_t in the definition (5.5) of viscometric flows is related to the frame-indifference of the stress in continuum mechanics. One can say that viscometric flows are plane Couette flows up to a time and space dependent change of frame. Some viscometric flows (plane Couette flow, in particular) are affine motions, and therefore have a favorable relation to the exact solutions of the equations of molecular dynamics given here. The reason that the full set of viscometric flows apparently does not have exact analogs in molecular dynamics is because of (1) the special nature of a simple fluid, which allows spatial dependence in \mathbf{Q}_t , and (2) the absence of full time-dependent frame

⁹ Most people these days would replace $\text{O}(3)$ by $\text{SO}(3)$, but this has no bearing on our arguments.

¹⁰ Proof: If $\mathbf{M}^2 = \mathbf{0}$, then $\mathbf{M}(\mathbf{M}(\mathbf{u})) = \mathbf{0}$ for all $\mathbf{u} \in \mathbb{R}^3$. Hence \mathbf{M} is not invertible, so \mathbf{M} has rank ≤ 2 . If \mathbf{M} has rank 2, then it nullifies a one-dimensional subspace. But then by $\mathbf{M}(\mathbf{M}(\mathbf{u})) = \mathbf{0}$ we must have that $\mathbf{M}\mathbf{u}$ belongs to that subspace. Thus, \mathbf{M} cannot be rank 2, for it would have a two-dimensional range. Thus, \mathbf{M} must have rank = 1, so $\mathbf{M} = \mathbf{a} \otimes \mathbf{b}$. Finally, $(\mathbf{a} \otimes \mathbf{b})^2 = \mathbf{0} \implies \mathbf{a} \cdot \mathbf{b} = 0$.

¹¹ For the rest of the paper we assume the domain for t excludes the isolated points (at most 3) where $\det(\mathbf{I} + t\mathbf{A}) = 0$.

indifference in molecular theory. The latter is closely related to the discussion surrounding (4.3) and (4.4). It is also related to the objections raised by Müller (1972). On the other hand, there are affine flows that are not viscometric flows. There are many such compressible flows, but also those given by (5.8) that would be possible in many incompressible materials. All have convenient interpretations at molecular level as exact solutions of the equations of molecular dynamics with an arbitrary number of simulated atoms satisfying arbitrary initial conditions. We do not understand why these other flows have been excluded from the definition of “viscometric flows”, or why they have not been used experimentally in the same way viscometric flows are used.

We close this subsection with a note about a known generalization of viscometric flows that is studied in the context of nonclassical fluids. These are *motions with constant stretch history*. In some cases they also have a favorable relation to the equations of motion. Noll (1962) shows that these motions can be represented by the following formula for the relative deformation gradient:

$$\mathbf{F}_t(\tau) = \mathbf{Q}(\tau)\mathbf{e}^{(\tau-t)\mathbf{M}}\mathbf{Q}^T(t), \tag{5.11}$$

where $\mathbf{M} \in \mathbb{R}^{3 \times 3}$, $\mathbf{Q} \in \text{O}(3)$, and all quantities are smooth in $-\infty < \tau \leq t < \infty$ and can depend on position $\mathbf{y} \in \mathbb{R}^3$, but the latter dependence is suppressed. Without loss of generality (Noll, 1962, Theorem 1) one can put $t = 0$ in this characterization. Also one can assume without loss of generality that $\mathbf{Q} \in \text{SO}(3)$, since it occurs twice in (5.11), i.e., if $\det \mathbf{Q}(t_0) = -1$ for some t_0 then $\det \mathbf{Q}(t) = -1$ for all t by continuity. If so, insert two $-I$'s in (5.11), which commute with every tensor, to make $\det \mathbf{Q}(t) = \det \mathbf{Q}(\tau) = 1$. Thus, smooth motions with constant stretch history are affine motions if and only if

$$\mathbf{I} + \tau \mathbf{A} = \mathbf{Q}(\tau)\mathbf{e}^{\tau \mathbf{M}}, \quad \mathbf{Q}(\tau) \in \text{SO}(3), \quad \tau \in \mathbb{R}. \tag{5.12}$$

Taking the determinant we have that $\det(\mathbf{I} + \tau \mathbf{A}) = \exp(\tau \text{tr} \mathbf{M})$. Since an exponential can be a cubic polynomial only if it is 1, this implies that \mathbf{A} has the representation (5.8). Furthermore, the 3×3 matrix \mathbf{M} has at least one real eigenvalue, so, operating (5.12) on the corresponding eigenvector $\hat{\mathbf{e}}$, we see that this eigenvalue is zero, so $\mathbf{A}\hat{\mathbf{e}} = \mathbf{M}\hat{\mathbf{e}} = 0$ and $\mathbf{Q}\hat{\mathbf{e}} = \hat{\mathbf{e}}$, i.e., \mathbf{Q} has constant axis, $\mathbf{Q}(\tau) = \exp(\theta(\tau)\mathbf{W})$, $\mathbf{W}^T = -\mathbf{W}$. Now writing the equation $\exp(-\tau \mathbf{M})(\mathbf{I} + \tau \mathbf{A}) = \mathbf{Q}(\tau)$ in the orthonormal basis $\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3 = \hat{\mathbf{e}}$, one finds first that $\mathbf{A} - \mathbf{M} = \gamma \mathbf{W}$, $\gamma = \theta'(0)$. Then putting the 11 and 22 components of $\exp(\tau \mathbf{M})(\mathbf{I} + \tau \mathbf{A})$ equal, the sum of 12 and 21 to zero, and the 31 and 32 components individually to zero, one proves that $\mathbf{A}^2 = 0$ and therefore the flow is viscometric. Hence, the remarks made above also apply to these more general motions.

5.3. Lees–Edwards and related methods

In this section we briefly explain that Lees and Edwards (1972) boundary conditions are precisely equivalent to OMD specialized to the case of plane Couette flow, and we point out that many of its generalizations are inconsistent with OMD.

5.3.1. Plane Couette flow

As noted above plane Couette flow is defined by (5.2) with $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ orthogonal and \mathbf{A} a trace-free matrix of rank one. Let $\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3$ be an orthonormal basis and let $\mathbf{A} = \dot{\gamma} \hat{\mathbf{e}}_1 \otimes \hat{\mathbf{e}}_2$ corresponding to plane Couette flow with a shear rate $\dot{\gamma}$. Let orthogonal dimensioned vectors be defined by $\mathbf{e}_i = L_i \hat{\mathbf{e}}_i$, $i = 1, 2, 3$. Following (5.2), an OMD simulation based on these choices is then defined, in the hatted basis, by

$$\mathbf{y}_{\mu,k}(t) = g_\mu(\mathbf{y}_k(t)) = \mathbf{y}_k(t) + \begin{pmatrix} \mu^1 L_1 + \mu^2 \dot{\gamma} t L_2 \\ \mu^2 L_2 \\ \mu^3 L_3 \end{pmatrix} \tag{5.13}$$

with μ^1, μ^2, μ^3 integers.

Picture $\hat{\mathbf{e}}_2$ oriented up and $\hat{\mathbf{e}}_1$ directed to the right. The Lees–Edwards method pictures a box $\Omega_0 = (0, L_1) \times (0, L_2) \times (0, L_3)$, fixed translates of this box in the $\pm \hat{\mathbf{e}}_1$ and $\pm \hat{\mathbf{e}}_3$ directions, and moving boxes above and below Ω_0 with center velocities depending linearly on the \hat{x}_2 coordinate. The MD simulation begins with a fixed number of atoms in Ω_0 with given initial positions and velocities. At every time-step positions of atoms are extended by the instantaneous periodicity to the other boxes. So far, this is clearly the same as the OMD method described above with the simulated atoms chosen as those belonging to Ω_0 . Let us suppose that an atom leaves the box Ω_0 at time t^* . In the Lees–Edwards method, if the k th atom leaves Ω_0 , say, through the left hand face, it is replaced by an atom at the right face using the \mathbf{e}_1 - periodicity. This occurs also in the formula (5.13), i.e.,

$$\mathbf{y}_{(1,0,0),k}(t^*) = \mathbf{y}_k(t^*) + \begin{pmatrix} L_1 \\ 0 \\ 0 \end{pmatrix}, \quad \dot{\mathbf{y}}_{(1,0,0),k}(t^*) = \dot{\mathbf{y}}_k(t^*). \tag{5.14}$$

If an atom leaves Ω_0 through the bottom face, then, in the Lees–Edwards method, it is replaced by an atom at the top face at a position determined by instantaneous periodicity, but with a horizontal velocity augmented by $\dot{\gamma} L_2$. This occurs also in

the formula (5.13), i.e.,

$$\mathbf{y}_{(0,1,0),k}(t^*) = \mathbf{y}_k(t^*) + \begin{pmatrix} \dot{\gamma} t^* L_2 \\ L_2 \\ 0 \end{pmatrix}, \quad \dot{\mathbf{y}}_{(0,1,0),k}(t^*) = \dot{\mathbf{y}}_k(t^*) + \begin{pmatrix} \dot{\gamma} L_2 \\ 0 \\ 0 \end{pmatrix}. \quad (5.15)$$

Thus, it is seen that the methods are equivalent.

The Lees–Edwards method shows that, in the case of plane Couette flow, one could redefine the simulated atoms of OMD at selected times so that they always lie in a fixed box. This is a special property of plane Couette flow,¹² and cannot be done in general for OMD, even when restricted to the time-dependent translation group. Possibly, it is for this reason that the more general viewpoint studied here was not noticed by people seeking generalizations of Lees–Edwards boundary conditions. However, all translation groups do have small unit cells, which can be taken as the parallelepiped generated by the three instantaneous vectors $(\mathbf{I} + t\mathbf{A})\mathbf{e}_i$, $i = 1, 2, 3$. As explained above, the simulated atoms could be redefined at occasional times to always lie in this deforming parallelepiped. After a long time, this parallelepiped necessarily becomes highly distorted. However, from the theory of *lattice invariant deformations* of crystallography (Pitteri and Zanzotto, 2002, Section 3.1), it is known that one could also occasionally redefine the unit cell so as to be relatively undistorted. If done correctly, all of these redefinitions would preserve our basic theorem that all the atoms satisfy exactly the equations of molecular dynamics¹³ at every $t > 0$. It should be mentioned that all the other discrete groups of isometries have fundamental domains which could be used in a similar way.

There is a vast literature on generalizations of Lees–Edwards boundary conditions. As far as we can tell, this literature is not based on the principle adopted here that all atoms satisfy exactly the equations of molecular dynamics. Motivation for these generalizations comes from the use of linear response theory and the Green–Kubo formula, approximate methods for time-dependent shear strain rates, and the use of soft loading or fictitious driving force fields. Some of the more widely studied versions include the DOLLS, SLLD, g-SLLD and p-SLLD algorithms. We do not present a comprehensive survey of this vast literature, but instead mention the two reviews (Evans and Morriss, 1990; Todd and Daivis, 2007). Again, we emphasize that the Lees–Edwards method is exact, while most if not all of these generalizations are not. Furthermore, as explained here, there are, however, a great many other exact methods of Lees–Edwards type, both by using other translation groups or some of the many other interesting isometry groups.

5.3.2. Elongational flows

It is clear from the literature described above that many people would like to simulate planar elongational flows, i.e., flows with Eulerian velocity gradient of the form

$$\nabla \mathbf{v} = \begin{pmatrix} \dot{\epsilon}(t) & 0 & 0 \\ 0 & -\dot{\epsilon}(t) & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (5.16)$$

In view of (5.7) this has a corresponding OMD interpretation if and only if $\mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}$ has this form. A short calculation shows that this has no nontrivial solution \mathbf{A} . Some of the examples of motions given by (5.8) have elongational character in the sense that, like (5.16), the velocity gradient is trace-free and rank-2. It would be interesting to invent a device to produce such flows, analogous to the numerous devices that have been invented to study elongational flows experimentally.

There is again a large literature on methods of molecular dynamics designed to simulate elongational flows (Baranyai and Cummings, 1999; Todd and Daivis, 1999, 2007; Frascoli et al., 2007; Hunt and Todd, 2003). Evidently, none of these are exact methods, though it is possible they give good approximations in situations of interest.

5.3.3. Parinello–Rahman method

The widely used method of Parrinello and Rahman (1980) and its generalizations also involves deforming boxes, like OMD in the case of the time-dependent translation group. The two methods differ in that the Parinello–Rahman method does not give exact solutions of the equations of molecular dynamics. Even when it happens that the unit cell of the Parinello–Rahman method is deforming according to the affine transformation $\mathbf{I} + t\mathbf{A}$, $\mathbf{A} \neq 0$, for a time interval, say, (t_1, t_2) , and the initial conditions of atoms coincide at t_1 , the two methods give different motions of the atoms. In that case the term added to the right hand side of the equations of molecular dynamics in the Parinello–Rahman method is

$$\mathbf{G}^{-1} \dot{\mathbf{G}} \dot{\mathbf{s}}_k \quad \text{where } \mathbf{G} = (\mathbf{I} + t\mathbf{A})^T (\mathbf{I} + t\mathbf{A}) \text{ and } \mathbf{s}_k(t) = (\mathbf{I} + t\mathbf{A})^{-1} \mathbf{y}_k(t). \quad (5.17)$$

¹² The point is that there is typically no box that remains the fundamental domain of the instantaneous translation group of an OMD simulation for an interval of time.

¹³ Lees and Edwards (1972) describe subtleties related to the conservation of momentum when switching between images in a discretized time-integration setting.

This does not generally vanish, as \mathbf{G} is invertible, $\dot{\mathbf{G}} = \mathbf{A} + \mathbf{A}^T + 2t\mathbf{A}^T\mathbf{A}$ vanishes at most at a single value of t , and $\dot{\mathbf{s}}_k$ is highly irregular. This should be contrasted with results given below for the Maxwell–Boltzmann equation and for Langevin dynamics: both cases represent dissipative theories that are precisely consistent with OMD.

It should be emphasized that the purpose of the two methods is also different: the Parinello–Rahman method and other isobaric methods are methods for finding equilibrium states at constant pressure, while OMD is a method for nonequilibrium molecular dynamics. OMD can only describe motions near macroscopic equilibrium if $|\mathbf{A}|$ is small, and can never describe the trend to equilibrium.

6. An exact reduction of the Maxwell–Boltzmann equation

The solutions of the equations of molecular dynamics described in Section 5 not only have a natural macroscopic interpretation as affine motions, but they also have a particular *statistics*. The distribution of velocities near one point determines the distribution near every other point. Thus, it is expected that these solutions have implications for mesoscale statistical theories.

6.1. An ansatz based on the statistics of objective molecular dynamics

The kinetic theory of gases involves a statistical averaging over velocity space, but not over position space or time intervals. These statistics are governed by the molecular density function $f: \mathbb{R} \times \mathbb{R}^3 \times \mathbb{R}^3 \rightarrow \mathbb{R}^{\geq}$. The number density of atoms at (t, \mathbf{y}) is $n(t, \mathbf{y}) = \int_{\mathbb{R}^3} f \, d\mathbf{v}$. The quantity $(1/n)f(t, \mathbf{y}, \mathbf{v})$ represents the probability density of finding an atom with velocity \mathbf{v} in a small neighborhood of \mathbf{y} at time t . In thinking about the statistics appropriate to the kinetic theory, one should consider a small volume centered at \mathbf{y} at time t and the velocities represented by atoms in that volume. To compare with the solutions found above, it is natural to take the volume to be that occupied by the simulated atoms, i.e., the fundamental domain FD, or one of the images of the FD under the group. So, in the heuristic statements below, we think of position space \mathbb{R}^3 partitioned into cells by a lattice based on the time dependent lattice vectors $(\mathbf{I} + t\mathbf{A})\mathbf{e}_i$, $i = 1, 2, 3$ (cf., Section 5). In this case we can take the FD as the unit cell $\mathcal{U}(t) = \{\lambda_i(\mathbf{I} + t\mathbf{A})\mathbf{e}_i : 0 \leq \lambda_1, \lambda_2, \lambda_3 < 1\}$. In the statements below, the “velocities at \mathbf{y} ” will be interpreted as the velocities in the instantaneous translate of $\mathcal{U}(t)$ containing \mathbf{y} . With this understanding and using (5.2), we have the following statements about the OMD solutions found above:

- The velocities at 0 are $\dot{\mathbf{y}}_i$, $i = 1, \dots, M$.
- The velocities at $\mathbf{y} = (\mathbf{I} + t\mathbf{A})\mathbf{x}$ are $\dot{\mathbf{y}}_i + \mathbf{A}\mathbf{x}$, $i = 1, \dots, M$.
- Or, in the Eulerian form used in the kinetic theory, the velocities at \mathbf{y} are $\dot{\mathbf{y}}_i + \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}$, $i = 1, \dots, M$.

From these statements we see that the probability of finding a velocity of the form $\mathbf{v} + \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}$ at \mathbf{y} is the same as the probability of finding a velocity \mathbf{v} at 0. This statement is independent of the value of M , independent of the initial conditions on the simulated atoms and independent of the force laws between atoms. In terms of the molecular density function,

$$f(t, \mathbf{y}, \mathbf{v} + \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}) = f(t, 0, \mathbf{v}), \quad (6.1)$$

or, rearranging,

$$f(t, \mathbf{y}, \mathbf{v}) = f(t, 0, \mathbf{v} - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}) = g(t, \mathbf{v} - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}), \quad \mathbf{v} \in \mathbb{R}^3, \mathbf{y} \in \mathbb{R}^3, t > 0. \quad (6.2)$$

We show that the ansatz (6.2) reduces the Maxwell–Boltzmann to an equation on $\mathbb{R} \times \mathbb{R}^3$. The Maxwell–Boltzmann equation is the following equation¹⁴ for the evolution of the molecular density function f :

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{y}} = \int_{\mathbb{R}^3} \int_S (f_* f' - f_* f) \, dS \, d\mathbf{v}_* \quad (6.3)$$

The notation is the following:

$$f_* = f(t, \mathbf{y}, \mathbf{v}_*) = f(t, \mathbf{y}, \mathbf{v}_* - ((\mathbf{v}_* - \mathbf{v}) \cdot \mathbf{e})\mathbf{e}),$$

$$f' = f(t, \mathbf{y}, \mathbf{v}') = f(t, \mathbf{y}, \mathbf{v} + ((\mathbf{v}_* - \mathbf{v}) \cdot \mathbf{e})\mathbf{e}),$$

$$f_* = f(t, \mathbf{y}, \mathbf{v}_*),$$

$$f = f(t, \mathbf{y}, \mathbf{v}), \quad (6.4)$$

¹⁴ We have omitted body forces in the Maxwell–Boltzmann equation, in keeping with the rest of this paper. Certain kinds of body forces could be included.

The integration $dS = dS(\theta, \zeta; |\mathbf{v}_* - \mathbf{v}|)$ on the right hand side of (6.3) is, more explicitly,

$$\int_S \dots dS = \int_0^{2\pi} \int_0^{\pi/2} \dots \sin\theta \mathbb{S}(\theta, |\mathbf{v}_* - \mathbf{v}|) d\theta d\zeta, \quad (6.5)$$

where \mathbb{S} is the scattering factor, and \mathbf{e} is a unit vector that depends on the hemispherical angles ζ, θ :

$$\mathbf{e} = \mathbf{e}(\zeta, \theta, \mathbf{v}_* - \mathbf{v}), \quad |\mathbf{e}| = 1. \quad (6.6)$$

It is therefore seen that the integrand on the right hand side of (6.3) is a function of $(r, \theta, \mathbf{v}_*; t, \mathbf{y}, \mathbf{v})$ with r, θ, \mathbf{v}_* being integrated out. All information about the atomic forces is contained in the form of \mathbf{e} , the domain S and the measure dS . The detailed form of $\mathbf{e}(r, \theta, \mathbf{v}_* - \mathbf{v})$ comes from the solution of the two-body problem.

Direct substitution of (6.2) into (6.3) and use of the identity $d/dt(\mathbf{M}^{-1}) = -\mathbf{M}^{-1}\dot{\mathbf{M}}\mathbf{M}^{-1}$ yields

$$\frac{\partial g}{\partial t} + \frac{\partial g}{\partial \mathbf{w}} \cdot [\mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{y} - (\mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{v})] = \int_{\mathbb{R}^3} \int_S (f_* f' - f_* f) |\mathbf{v}_* - \mathbf{v}| dS d\mathbf{v}_* \quad (6.7)$$

with g being evaluated at the arguments $t, \mathbf{v} - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{y}$. On the right hand side of (6.7), using the change of variables $\mathbf{w}_* = \mathbf{v}_* - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{y}$ we have

$$\int_{\mathbb{R}^3} \int_S (f_* f' - f_* f) |\mathbf{v}_* - \mathbf{v}| dS d\mathbf{v}_* = \int_{\mathbb{R}^3} \int_S (g_* g' - g_* g) |\mathbf{w}_* - \mathbf{w}| dS d\mathbf{w}_* \Big|_{\mathbf{w} = \mathbf{v} - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{y}} \quad (6.8)$$

Replacing $\mathbf{v} - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{y}$ by \mathbf{w} throughout (6.7), (6.8), we have that $g(t, \mathbf{w})$ satisfies the equation

$$\frac{\partial g}{\partial t} - \frac{\partial g}{\partial \mathbf{w}} \cdot \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{w} = \int_{\mathbb{R}^3} \int_S (g_* g' - g_* g) |\mathbf{w}_* - \mathbf{w}| dS d\mathbf{w}_* \quad (6.9)$$

Hence, under the ansatz (6.2), the Maxwell–Boltzmann equation is reduced to an equation in only the independent variables (t, \mathbf{w}) , effectively removing the spatial dependence.

6.2. H-theorem

It is interesting to look at the H-theorem corresponding to these solutions. The easiest way to derive it is to write down its standard form for the original molecular density function f and then to change variables.

For our purposes it is more useful to look at (minus the) entropy per volume than the entropy per molecule. Therefore we put

$$H(t, \mathbf{y}) = \int_{\mathbb{R}^3} f \log f d\mathbf{v}, \quad (6.10)$$

(Boltzmann's "H" is $(1/n)H$, where $n = \int_{\mathbb{R}^3} f d\mathbf{v}$). Following the standard approach we multiply (6.3) by $\log f$ and integrate over $\mathbf{v} \in \mathbb{R}^3$. We have formally, by the usual argument,

$$\frac{\partial H}{\partial t} + \text{div}_{\mathbf{y}} \int_{\mathbb{R}^3} \mathbf{v} f \log f d\mathbf{v} \leq 0, \quad (6.11)$$

the inequality on the right arising from the special form of the collisions operator and the monotonicity of the log function. In these calculations use is made of the balance of mass, i.e., the 0th moment of the Maxwell–Boltzmann equation.

Now we substitute $f(t, \mathbf{y}, \mathbf{v}) = g(t, \mathbf{v} - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1} \mathbf{y})$ into (6.11) and change variables. Trivially,

$$H(t, \mathbf{y}) = \int_{\mathbb{R}^3} f \log f d\mathbf{v} = \int_{\mathbb{R}^3} g \log g d\mathbf{w}, \quad (6.12)$$

while (6.11) becomes simply,

$$\frac{\partial H}{\partial t} + \text{tr}(\mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}) H \leq 0. \quad (6.13)$$

Note that the expansion rate $\text{tr}(\mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1})$ enters in a simple way. For isochoric motions such as plane Couette flows, we have simply that H is decreasing.

6.3. Discussion

It would be extremely interesting to deduce information about the form of g satisfying (6.9) for general force laws. Forthcoming work (James and Müller) shows that some information on the time-dependence of g can be found in a special case.

In general, one cannot expect any simple kind of statistics for nonequilibrium flows, even for moderately rarefied monatomic gases. That is evident from the fact that the Maxwell–Boltzmann equation is an infinite dimensional dynamical system which produces solutions from general initial data $f(0, \mathbf{y}, \mathbf{v})$ (DiPerna and Lions, 1989). However, for the reduced equations given here, there is some reason to believe that there may be relatively simple asymptotic solutions, or a simple asymptotic equation. If these could be found, it might be possible to infer a statistics in general for affine motions in general

materials, in the same way the canonical distribution of statistical mechanics can be inferred from the Maxwellian density (i.e., replace $(\frac{1}{2})|\mathbf{v}|^2$ by a general Hamiltonian) in the case of equilibrium. Our simulations presented in Section 8, albeit for a more complex situation, support the idea that these statistics would depend on the form of the atomic forces, even though the ansatz does not.

There are some known solutions for the infinite set of equations of the moments of the Maxwell–Boltzmann equation (Ikenberry and Truesdell, 1956; Truesdell, 1956) for inverse 5th power molecules. It is not known if these correspond to a nonnegative molecular density function. These all apparently fall under the ansatz given above. Explicit solutions for various second and third moments, the stress and heat flux, are given in the case of plane Couette in Truesdell (1956) (see also Truesdell and Muncaster, 1980, Chapter XIV). These have the following structure. They consist of the sum of an oscillatory part multiplied by a decaying exponential and an exponentially increasing part. The decaying part can be eliminated by choosing special initial conditions. All the interesting properties of the solution—viscosities, normal stresses—are interpreted from the exponentially increasing part. Since moments are linear functions of the molecular density function, this hints at the possibility of a relatively simple asymptotic form of Eq. (6.9). The only other exact solution of the Maxwell–Boltzmann equation of which we are aware is that of Bobylev (1976, 1977) (independently, Krook and Wu, 1976, 1977), also for inverse 5th power molecules, but this solution describes a trend to equilibrium and therefore could not be directly related to the OMD solutions.

The reduced H -theorem (6.13) gives some heuristic qualitative information on how such a molecular density function should behave.¹⁵ Consider the case that the expansion rate $\text{tr}(\mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}) = 0$ for simplicity. Recalling that $H = \int g \log g \, d\mathbf{w}$, and noting that the function $x \log x$ is bounded from below and has a single minimum at $x = e^{-1}$, we assume first that $g(t, \cdot)$ has compact support independent of t . Then, since $g \log g$ is bounded from below, and H is decreasing, one expects that dH/dt tends asymptotically to 0. But in that case, from standard calculations in the kinetic theory, the collisions operator on g would be asymptotically zero, and so g would be asymptotically Maxwellian. This is highly unexpected; rather, these solutions are expected to lead to functions H that tend to $-\infty$ as $t \rightarrow \infty$. It is seen that such a decrease is consistent with $H = \int g \log g \, d\mathbf{w}$ for appropriate g that do not have fixed compact support. For example, if $g(t, \mathbf{v}) = \varepsilon^3(t)$ on a ball of radius $1/\varepsilon(t)$, and is zero otherwise, then the number density $n(t) = \int g \, d\mathbf{w}$ is constant, but

$$H(t) = \int_{B_{1/\varepsilon(t)}} \varepsilon^3(t) \log \varepsilon^3(t) \, d\mathbf{w} = 4\pi \log \varepsilon(t) \rightarrow -\infty, \quad (6.14)$$

if $\varepsilon(t) \rightarrow 0$. This suggests that the sought after molecular density functions tend to zero, possibly uniformly, and have a spreading support with substantial support at higher and higher speeds. This is consistent with the physical intuition that external work is being done on the material at the boundaries and dissipation leads to an unbounded increase in the temperature at long times.

The OMD solutions described above are applicable to arbitrary kinds of atoms, and therefore to kinetic theories of gas mixtures, as described for example by Garzó and Santos (2003). It would be interesting to examine these more general theories in the present context. These authors also observe that the ansatz $f(t, \mathbf{y}, \mathbf{v}) = g(t, \mathbf{v} - \mathbf{C}\mathbf{y})$ reduces the Maxwell–Boltzmann equation, as is immediately clear. This agrees with the present ansatz only when $\mathbf{C} = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}$ is independent of t . A short calculation shows that $\mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}$ is independent of t if and only if $\mathbf{A}^2 = 0$, which by footnote 10 is equivalent to $\mathbf{A} = \mathbf{a} \otimes \mathbf{b}$, $\mathbf{a} \cdot \mathbf{b} = 0$. This gives $\mathbf{C} = \mathbf{a} \otimes \mathbf{b}$ and corresponds to plane Couette flow. For \mathbf{C} not of this form we have no OMD interpretation of these flows, possibly indicating a discrepancy between kinetic theory and molecular dynamics.

7. Proposed extension of the principle of material frame indifference

The calculations of the preceding section, albeit restricted to the very special situation of moderately rarefied monatomic gases, suggest that the OMD solutions given in Section 5 are representative of material behavior. The OMD solutions of Section 5 are possible in any material with an arbitrary number of simulated atoms having arbitrary initial conditions, under very mild conditions on the force formula. The presence of these solutions is a direct consequence of the frame-indifference (actually just translation invariance) and permutation invariance of this formula. In all cases the macroscopic motions corresponding to these OMD solutions are affine motions, independent of the material, and each affine motion corresponds to an infinity of OMD solutions, with an arbitrary number of simulated atoms satisfying arbitrary initial conditions. This suggests that the principle of material frame indifference of nonlinear continuum mechanics should be augmented to include the requirement that the balance laws of continuum mechanics hold for such motions. This becomes a restriction on constitutive relations, as discussed below.

The principle of material frame-indifference is the following (Truesdell and Noll, 2004, pp. XI and 296). One defines a *change of frame* by the equations

$$\mathbf{y}^* = \mathbf{R}(t)\mathbf{y} + \mathbf{c}(t), \quad (7.1)$$

¹⁵ This paragraph benefited from discussions with Stefan Müller.

where $\mathbf{R} : [0, \infty) \rightarrow \text{SO}(3)$ and $\mathbf{c} : [0, \infty) \rightarrow \mathbb{R}^3$, assumed to be smooth functions. For the Lagrangian description of motion $\mathbf{y}(t, \mathbf{x})$, $\mathbf{x} \in \Omega$, $t > 0$, for example, we have for an observer in the starred frame,

$$\mathbf{y}^*(t, \mathbf{x}) = \mathbf{R}(t)\mathbf{y}(t, \mathbf{x}) + \mathbf{c}(t). \quad (7.2)$$

All transformation laws for kinematic quantities come from this relation. Other macroscopic quantities are assumed to have transformation laws. The Cauchy stress for example has the transformation law for an objective tensor:

$$\sigma^* = \mathbf{R}(t)\sigma\mathbf{R}(t)^T. \quad (7.3)$$

In a purely mechanical setting a constitutive equation is given that relates the Cauchy stress to kinematic quantities. Simple fluids as described above are examples. More generally, $\sigma(t, \mathbf{x}) = f_{t,\mathbf{x}}(\mathbf{y})$, where $f_{t,\mathbf{x}}$ for each $t > 0$, $\mathbf{x} \in \Omega$ is a functional defined on a space of histories $\mathbf{y}(\mathbf{z}, s)$, $\mathbf{z} \in \Omega$, $s < t$. The principle of material frame indifference states the functional f is independent of the observer in the sense that

$$\sigma^*(t, \mathbf{x}) = f_{t,\mathbf{x}}(\mathbf{y}^*) \quad \text{if and only if} \quad \sigma(t, \mathbf{x}) = f_{t,\mathbf{x}}(\mathbf{y}), \quad (7.4)$$

where σ^* and \mathbf{y}^* are related to σ and \mathbf{y} by (7.3) and (7.2), respectively. The point is that $f_{t,\mathbf{x}}$ is the same functional in the two statements in (7.4). This is the main principle that is used to give the accepted forms of the constitutive equations for Newtonian and non-Newtonian fluids, nonlinearly elastic solids, viscoelastic solids, etc., from rather general starting assumptions.

The added requirement that is suggested by this paper, as discussed above, is

The equations of motion are identically satisfied for the family of affine motions $\mathbf{y}(t, \mathbf{x}) = (\mathbf{I} + t\mathbf{A})\mathbf{x}$, $\mathbf{x} \in \Omega$ for $t \in \mathbb{R}$ such that $\det(\mathbf{I} + \mathbf{A}t) > 0$.

In Eulerian form the suggested modification is:

The equations of motion are identically satisfied for the family of velocity fields $\mathbf{v}(t, \mathbf{y}) = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}$, $\mathbf{y} \in \mathbf{y}(\Omega, t)$, for $t \in \mathbb{R}$ such that $\det(\mathbf{I} + \mathbf{A}t) > 0$.

The modified principle is only meant to apply to homogeneous materials, as for example would be associated with the method of OMD simulation using the translation group, as described above. For incompressible materials we would of course impose the constraint of incompressibility on the affine motions.

All generally successful constitutive equations we know satisfy the augmented principle. However, in other mesoscale theories which have a relation to molecular dynamics, it seems to be a useful restriction. We discuss some implications.

1. The modified principle is satisfied for all simple fluids by virtue of the calculation (5.10) and the form of the constitutive relations for these materials. Thus, the modified principle is satisfied for all (homogeneous) Newtonian and non-Newtonian fluids and all nonlinearly elastic solids. All models of viscoelastic fluids of which we are aware satisfy the modified principle.
2. It is interesting to look at the extended principle for models of turbulence. Mathematically, one could imagine a possible violation, as turbulence models often involve spatial averaging of nonlinear quantities. We consider in detail at the LES (large eddy simulation) and related models (Pope, 2000; Smagorinsky, 1963). LES is based on the equations for the Eulerian velocity of the following form:

$$\bar{\mathbf{v}}_t + \nabla \bar{\mathbf{v}} \bar{\mathbf{v}} = -\nabla \bar{P} + \nu \Delta \bar{\mathbf{v}} - \nabla \cdot \tau, \quad \nabla \cdot \bar{\mathbf{v}} = 0, \quad (7.5)$$

where P is the average kinematic pressure, ν is the kinematic viscosity, the overbar denotes spatial filtering,

$$\bar{\mathbf{u}}(t, \mathbf{y}) = \int_{\mathbb{R}^3} g(\mathbf{y} - \mathbf{y}') \mathbf{u}(t, \mathbf{y}') d\mathbf{y}', \quad (7.6)$$

and

$$\tau = \bar{\mathbf{v}} \otimes \bar{\mathbf{v}} - \bar{\mathbf{v}} \otimes \bar{\mathbf{v}}. \quad (7.7)$$

It is a straightforward exercise to show that indeed all isochoric affine motions $\mathbf{v}(t, \mathbf{y}) = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{y}$ identically satisfy (7.5) if the first moment of g vanishes and $\int g d\mathbf{y} = 1$. The Navier–Stokes alpha model (Foias et al., 2001) also satisfies the modified principle under the same restrictions on the filter. It is more difficult to make such statements about the $k-\varepsilon$ model of turbulence, because the constraints on initial conditions on the functions k and ε that appear in that model are not clear. If affine motions are assumed to be solutions of the $k-\varepsilon$ model regardless of these initial conditions, it follows that $k-\varepsilon$ models do not satisfy the modified principle. If, on the other hand, one is allowed to adjust initial conditions in any way, then, at least in the case of simple shearing one does have satisfaction of the modified principle for at least short times. Turned around, the suggested modification suggests how to choose initial conditions for the $k-\varepsilon$ model, at least for these special flows.

3. The Langevin equation as usually written for plane Couette flows satisfies reasonable interpretation of the principle, and the principle gives a suggestion on how to write Langevin dynamics for more general flows. For definiteness we restrict attention to the case of a polymer solution with coarse-grained polymer chains represented by a string of beads at

positions $\mathbf{X}_{v,k}$, $v \in \mathbb{Z}^3$, $k = 1, \dots, M$ each with effective mass m in a plane Couette flow with velocity $\mathbf{v}(\mathbf{X}) = \dot{\gamma} X_2 \mathbf{e}_1$, $\dot{\gamma} = \text{const.}$, and $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ is an orthonormal basis. The beads interact according to a potential energy $\varphi(\dots, \mathbf{X}_{v_1,1}, \dots, \mathbf{X}_{v_1,M}, \mathbf{X}_{v_2,1}, \dots, \mathbf{X}_{v_2,M}, \dots)$ whose derivative is assumed to be frame-indifferent and permutation invariant in the sense of (3.2), (3.3). The stochastic terms then model the effects of the solvent on the motions of these beads. As above, we write $\mathbf{X}_k = \mathbf{X}_{(0,0,0),k}$, $k = 1, \dots, M$, and assume that $\mathbf{X}_k = \mathbf{X}_k(t)$ satisfy the Langevin equations,

$$m\ddot{\mathbf{X}}_k = \frac{\partial \varphi}{\partial \mathbf{X}_{(0,0,0),k}} - \gamma m(\dot{\mathbf{X}}_k - \dot{\gamma}(\mathbf{X}_k \cdot \mathbf{e}_2)\mathbf{e}_1) + R_k, \quad (7.8)$$

where R_k is a stochastic term which is a stationary Gaussian process with zero mean,

$$\langle R(t) \rangle = 0, \quad \langle R(t) \cdot R(t') \rangle = 2\gamma k_B T m \delta(t - t'), \quad (7.9)$$

and δ is a Dirac mass, k_B is Boltzmann's constant, T is the target temperature, γ is the damping constant. The precise interpretation of (7.8), (7.9) is in terms of stochastic ordinary differential equations.

For general affine flows we suggest writing the Langevin equation as

$$m\ddot{\mathbf{X}}_k = \frac{\partial \varphi}{\partial \mathbf{X}_{(0,0,0),k}} - \gamma m(\dot{\mathbf{X}}_k - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{X}_k) + R_k \quad (7.10)$$

which reduces to (7.8) in the case of plane Couette flows, $\mathbf{A} = \dot{\gamma} \mathbf{e}_1 \otimes \mathbf{e}_2$.

A reasonable interpretation of the principle is that the remaining beads with positions

$$\mathbf{X}_{v,k}(t) = \mathbf{X}_k(t) + (\mathbf{I} + t\mathbf{A})v^i \mathbf{e}_i, \quad (7.11)$$

also then necessarily satisfy the Langevin equations. We are relying on the ideas that (1) the beads represent some kind of average positions of atoms on polymer chains, or are simply Lagrangian markers for the chain, (2) that the Langevin solution corresponds to an OMD solution carried out for all the atoms, including the atoms of the solvent. Now using the frame-indifference and permutation invariance of φ and (3.9), (7.11), we have by direct calculation

$$m\ddot{\mathbf{X}}_{v,k} = m\ddot{\mathbf{X}}_k = \frac{\partial \varphi}{\partial \mathbf{X}_{(0,0,0),k}} - \gamma m\dot{\mathbf{X}}_k + R_k = \frac{\partial \varphi}{\partial \mathbf{X}_{v,k}} - \gamma m(\dot{\mathbf{X}}_{v,k} - \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{X}_{v,k}) + R_k. \quad (7.12)$$

Hence, the other atoms $\mathbf{X}_{v,k}$, $v \neq (0,0,0)$ then necessarily exactly satisfy the equations of Langevin dynamics. A key point in this argument is that the noise term R_k is independent of v . This is also consistent with the statistics given in the three bullets of Section 6.1, though more general forms of R_k than (7.9) could be considered. (This statistics should be considered as a requirement to be satisfied by the form of the noise (7.9)). In the same way that OMD gives a simplified method of simulating molecular dynamics for affine flows, the above gives a simplified exact method of simulating Langevin dynamics for these flows.

As many people have noticed, the Langevin equation is similar to thermostatted equations of motion. We conclude this section with a few remarks about thermostats. It is easily seen that under the restrictions (a) there is no time-dependence of the group elements, and (b) the group is finite (N is finite), if the simulated atoms $(1,k)$, $k = 1, \dots, M$ satisfy the Nosé–Hoover thermostatted equations of motion, then all the atoms satisfy the Nosé–Hoover thermostatted equations of motion. This statement is not true for all thermostats. Some of them add a nonlinear term in the momentum vector on the right hand side of the equations of motion, and, for all of these that we have seen, the above statement is not true. The restriction to finite N here may only be a formality related to the convergence of a sum appearing in the thermostat model: we did not investigate whether there is a version of the Nosé–Hoover thermostat that applies only to the atoms in the FD. For the time-dependent groups the statement above does not hold: all thermostats of which we are aware do not preserve the time-dependent invariant manifold of molecular dynamics when the time dependence is not trivial.

These statements suggest that the Langevin equation, while perhaps more restricted in its application, is more faithful to molecular dynamics than thermostatted equations of motion. The main point is the inclusion of the term involving the macroscopic motion into the Langevin equation. While we know of no justification to use thermostat models away from macroscopic equilibrium, it is possible that the inclusion of similar terms into the Nosé–Hoover or other thermostats will then make the modified thermostats compatible with the method proposed here.

8. Study of the failure of carbon nanotubes under imposed strain rate

A rather different application of OMD is to the deformation and failure of nanostructures. Here we give a simple demonstration of the method by studying the deformation and failure of carbon nanotubes pulled axially at a constant macroscopic strain rate.

We refer to Section 2 for the groups used. As explained there, we first used the group $G_4 = \{h^p g^q f^m : p \in \mathbb{Z}, q = 1, \dots, n, m = 1, 2\}$ to construct the positions of a nominally unstressed (6,6) nanotube (see Dumitrică et al., 2006), with h, g, f defined in Items 1, 2, 3 following (2.3) (except θ is a rational multiple of 2π). Note also the comments in the latter part of

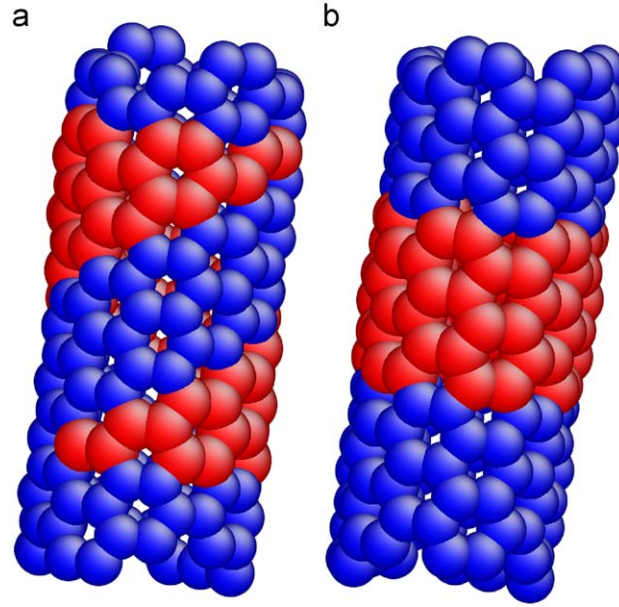


Fig. 3. The two sets of simulated atoms (in red) corresponding to the two subgroups used in the simulations, showing the initial positions (acknowledgment, Li, 2003). (a) $p' = 12$, $q' = 3$; (b) $p' = 6$, $q' = 6$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Section 2. The choice of parameters was

$$\begin{aligned} \mathbf{x}_0 &= (0, 0, 0), \quad \mathbf{e} = (0, 0, 1), \quad \tau_0 = 0.123 \text{ nm}, \quad \theta = \pi/6, \\ \mathbf{e}_1 &= (0.98481, 0.17365, 0), \quad \psi = \pi/3, \quad n = 6, \quad \xi = 0. \end{aligned} \quad (8.1)$$

We applied this group to the point $\mathbf{z}_1 = (0.4068 \text{ nm}, 0, 0)$ to generate a full nanotube.

Then, as explained in Section 2, we considered subgroups $G' \subset G$ and corresponding sets of simulated atoms belonging to the fundamental domains of these subgroups, the initial positions of the simulated atoms given by the positions of the nominally relaxed nanotube described above. In all simulations we used two different subgroups and corresponding FDs. These effectively defined the simulated atoms. In the notation of Section 2 these are specified by

$$p' = 12, q' = 3 \quad \text{and} \quad p' = 6, q' = 6. \quad (8.2)$$

Pictures of the two FDs and corresponding simulated atoms in red are shown in Fig. 3. The FD on the left of Fig. 3 was particularly chosen to promote the formation of Stone–Wales defects. This FD is consistent with the possibility of a series of widely spaced Stone–Wales defects on two infinite intertwined helices propagating so as to cause plastic slip on these helices.

Temperature is calculated as the mean kinetic energy of simulated atoms, after subtracting off the average velocity, converted to thermal units, i.e., using the formula

$$T(t) = \frac{m}{3k_B M} \sum_{k=1}^M \left| \dot{\mathbf{y}}_k(t) - \frac{1}{M} \sum_{i=1}^M \dot{\mathbf{y}}_i(t) \right|^2, \quad (8.3)$$

where $k_B = 8.617343 \times 10^{-5} \text{ eV/K}$ is Boltzmann's constant and $m = 0.124371 \text{ eV}/(\text{nm/ps})^2$ is the mass of C.

These initial positions, together with initial velocities having zero angular velocity (see Section 2), gave solutions showing a transient which depended on the details of the initial conditions. We found that macroscopic quantities like failure strain and temperature vs. time were reproducible if we began from initial positions and velocities taken after this transient. Our procedure was to set the strain rate $\dot{\epsilon} = 0$, so $\tau = \tau_0$ (cf., (8.1)), to begin with random initial velocities modified to have zero angular velocity and scaled to approximate a certain temperature, and to run a simulation for 10^6 fs. We monitored the transient by plotting the temperature vs. time, and in all cases found a nearly constant temperature vs. time profile well before the end of this preliminary simulation. Positions and velocities as initial conditions for subsequent simulations were taken from near the end of this simulation. Subsequent simulations were done of course with nonzero strain rate. Following this procedure, we did several simulations chosen with the same initial temperature and strain rate, but with rather different details of initial conditions, and found that failure strains varied by less than 1% in all cases. This was true with both FDs and otherwise no significant differences were seen between simulations with one FD or the other. This reproducibility was striking in view of the dramatic effect of strain rate and initial temperature as reported below.

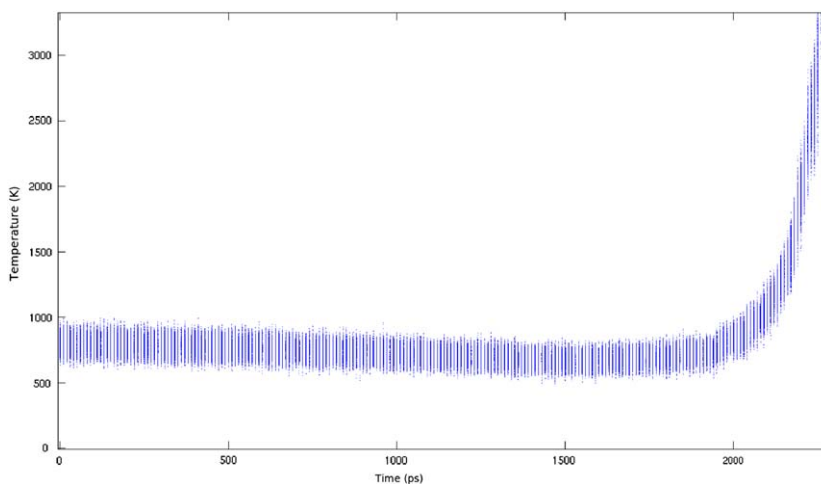


Fig. 4. Temperature vs time. Initial temperature = 800 K, strain rate = 10^8 s^{-1} , 2.5×10^6 time steps, FD is (b) of Fig. 3.

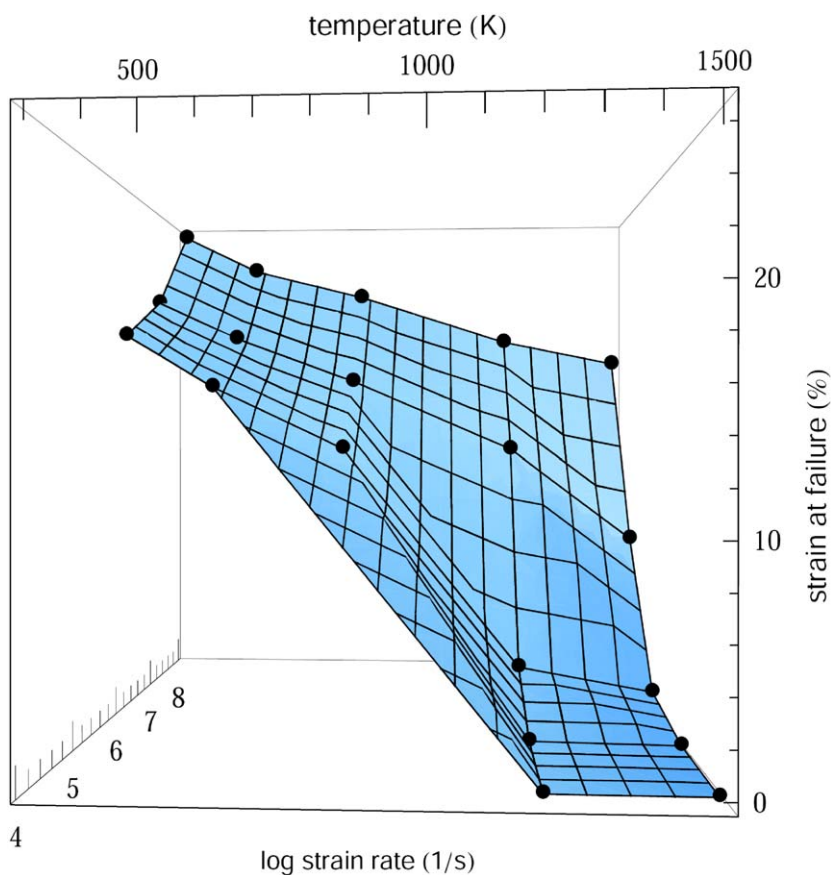


Fig. 5. Failure strain vs. initial temperature and log strain rate from a large set of simulations. For each point at least two simulations were run with the two different fundamental domains: the strain at failure differed by less than 1%.

Modes of failure varied widely. At the very highest strain rates we saw (a) fibrous fracture, in which the nanotube split axially into two parallel fibers with part of the simulated atoms on one and part on the other,¹⁶ (b) cavitation, in which a hole opened up in the side of the nanotube, (c) cross-sectional collapse, in which the tube collapsed into two parallel

¹⁶ This is perfectly fine vis-a-vis the basic theory.

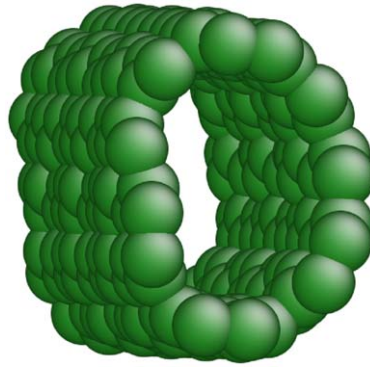


Fig. 6. Extreme distortion of the cross-section in low failure strain calculations.

graphene sheets. However, the most common mode of failure could be described as melting, in which there was sudden widespread loss of coordination. This was especially true at the lower strain rates. However, we did not see any Stone–Wales defects in any of the simulations. Just prior to failure we did sometimes see what could be termed Stone–Wales partials, in which one 6 membered ring donated an atom to a neighbor, resulting in contiguous 7 and 5 membered rings. The varied modes of failure at the highest strain rates would seem to suggest that the hypotheses of transition state theory are not being satisfied in those cases. A study by Wei et al. (2003) of the failure of carbon nanotubes at various strain rates and temperatures based on transition state theory gives strains at failure qualitatively different from that reported here. This is also true of the earlier study of Jakobson et al. (1997), which is partly based on a similar method but not using transition state theory.

A typical temperature vs. time plot is seen in Fig. 4. Except in simulations that exhibited failure very quickly, temperature vs. time showed a long period with a negative slope, interpretable as the thermoelastic effect. In this sense we find that (6,6) C nanotubes behave more like crystals than polymers: entropic effects are apparently confined to “lattice” vibrations. Well prior to actual failure, and not evident by looking at movies of the simulations, the graph of temperature vs. time begins increasing rapidly.

The simulation corresponding to Fig. 4 showed no Stone–Wales partials, as far as we could tell. Three snapshots from this simulation are shown in Fig. 2. Fig. 2c shows a cavitation failure at about 2240 ps: a series of holes opened up in the side of the nanotube, each bounded by 18 atoms. Soon after that, at about 2260 ps, the cross-section collapsed, leaving two approximately parallel graphene strips. A catastrophic loss of coordination occurred shortly thereafter.

Most of the simulations exhibited a clearly defined failure strain, resulting in complete loss of coordination. A plot of failure strain vs. strain rate and initial temperature is shown in Fig. 5. This exhibits a rather sharp drop at strain rate of about 10^7 s^{-1} and a temperatures of about 1200 K. This is quite opposite to the conventional wisdom that lower strain rates and higher temperatures promote ductility. However, since we have seen neither Stone–Wales defects nor any other analog of dislocations, perhaps one should think in terms of rather different mechanisms of failure at these rates.

The failures at low strain rates and higher temperatures in Fig. 5, resulting in exceptionally low strain at failure, were preceded by large amplitude vibrations of the cross-section (Fig. 6). While these were not precisely periodic, they occurred at a frequency of approximately 100 GHz. It would be interesting to examine experimentally the effect of radiation of these frequencies on failure.

Here we have concentrated on the behavior of near perfect nanotubes to demonstrate that the method can predict failure, and for its inherent interest. In future studies we plan to parallelize the method so as to access lower strain rates, to explore the effect of removing one or more atoms, to investigate the behavior of nanotubes with different chirality, to examine the effects of pre-stretch and pre-twist, and to implement groups that impose both shear and elongation.

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